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The Action of Sulfur on p-Toluidine: Some New Derivatives of Thio- and Dithio-p-Toluidine

DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE OF COLUMBIA UNIVERSITY

By

LEONARD SMIDTH, B.A., M.A.

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New York, N. Y.
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TO MY MOTHER

ACKNOWLEDGMENT

The author wishes to express his appreciation to Professor Marston Taylor Bogert for his helpful suggestions and his kindly criticisms of this research. He also feels greatly indebted to the E. I. Du Pont de Nemours & Co. for the fellowship under which part of this work was carried out.

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The Action of Sulfur on p-Toluidine: Some New Derivatives of Thio- and Dithio-p-Toluidine

Abstract

In spite of the amount of work that has been done on the action of sulfur on primary aromatic amines, very little is known about the course of the reactions involved. Such fusions are generally accompanied by much tarry and resinous materials, hard to identify, and making such reactions difficult to follow. The purpose of this investigation was to study the action of sulfur on *p*-toluidine with a view to learn more about the reaction in which thio- and dithio-*p*-toluidine are formed, and their relation to the important dye intermediate, dehydrothio-*p*-toluidine. It was hoped that we could convert some product of the fusion directly or indirectly into the latter, and thus find a better method of preparation than the present one.

The thio- and dithio-*p*-toluidine used in this work were prepared by fusing sulfur with *p*-toluidine in the presence of litharge, according to the directions of Bogert and Mandelbaum, but at a slightly lower temperature (130–140°). The products of the fusion, however, were separated in a new way by fractional neutralization, a method much easier and less expensive than the one developed by the latter. Considerable time was spent in trying to isolate new compounds from the tarry by-products, dehydrothio-*p*-toluidine being isolated in small yield.

The course of the reaction was studied by following the yields of products obtained when the fusion was carried out at different temperatures, and when different concentrations of starting materials were used. At higher temperatures (above 145°) and also with higher concentrations of sulfur more tarry by-products were formed with a corresponding decrease in the amounts of the other products. With lower concentrations of sulfur the yields of thio-*p*-toluidine were slightly increased but the amounts of unchanged *p*-toluidine were always quite large. A temperature of 130–140° was found to be the optimum one

for obtaining both the mono- and disulfide. Further insight into the course of the reaction was obtained by fusing thio- or dithio-*p*-toluidine with sulfur, *p*-toluidine, and litharge either individually or combined. From the results obtained, it does not seem probable that the reaction of sulfur on *p*-toluidine proceeds in the same way as that of sulfur on aniline.

Two series of derivatives were prepared from the mono- and disulfide isolated in the above fusions. With thio-*p*-toluidine, methods were worked out for replacing the amino groups with chlorine and iodine. In the case of the bromine derivative, only one amino group was replaced by a bromine, the other being replaced by a hydrogen. These resinous compounds were then oxidized to the solid sulfones. By the action of concentrated hydrochloric acid on the diazonium chloride, an unusual replacement took place, and a complex ether formed. A sulfoxide was prepared by oxidizing the acetyl derivative of thio-*p*-toluidine with hydrogen peroxide.

From the disulfide the zinc salt of *o*-amino *m*-thiocresol was obtained, and by fusing it with ortho- and meta-nitrobenzoyl chloride, we prepared the nitrobenzothiazoles and from them the analogous dehydrothiotoluidines. Attempts were made to prepare dyes similar to Columbia Yellow by sulfonation of the latter and then hypochlorite oxidation of the sodium salts. The ortho compound did not give a dye and indications are that oxidation did not take place. The meta compound gave a similar dye to Columbia Yellow, but of a lighter shade.

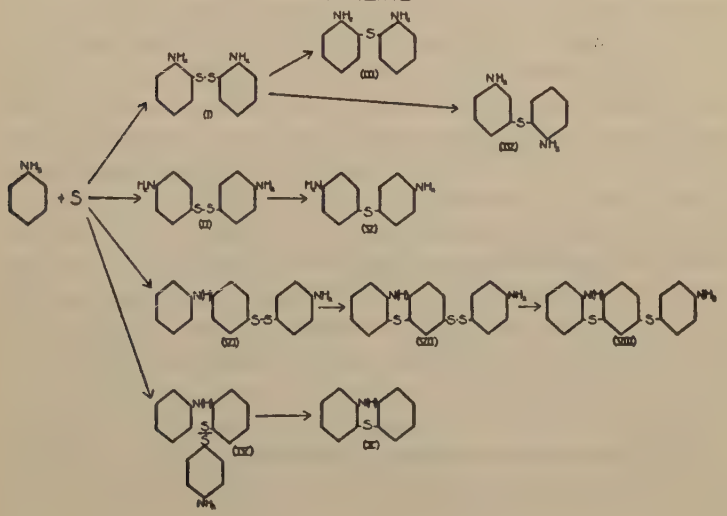
The following new substances were prepared in the course of the work:

Bis[2(2′-chlor-5′-methylphenyl sulfide)-4-methylphenyl] oxide.
Bis(2-iodo-5-methylphenyl)sulfone.
Bis(2-chlor-5-methylphenyl)sulfone.
2-Brom-bis(methylphenyl)sulfone.
Bis(2-acetamino-5-methylphenyl)sulfoxide.
2(*m*-Nitro phenyl) 6-methyl benzothiazole.
2(*m*-Amino phenyl) 6-methyl benzothiazole.
2(*o*-Amino phenyl) 6-methyl benzothiazole.
2(*o*-Acetamino phenyl) 6-methyl benzothiazole.

Introductory and Historical

Merz and Weith[1] in their pioneering work discovered that sulfur acted upon aniline and were able to isolate a crystalline substance from the fusion products which they called thioaniline. By using litharge,[2] they found that the reaction could be carried out at a lower temperature and that the amount of resinous material formed was decreased. K. A. Hoffman[8] found that when sulfur was heated alone with aniline for 12 hours at 170–180°, a di-*o*-thioaniline (I) was obtained, while he noticed the much greater velocity of the action when hydrochloric acid was present, with the formation, however, of a di-*p*-thioaniline (II). Hinsberg[12] found the last reaction to be not quite so simple as stated by Hoffman, but, under the conditions observed by the latter author, to give at least four substances, namely, diphenylamine, Merz's thioaniline (V), a dithio aniline, and a new thioaniline which he took to be the unsymmetrical compound (IV). Again, Hoffman[10] found that when aniline, sulfur and hydrochloric acid were heated together in a certain proportion, first for an hour at 170° and then for a further five hours at 200°, the principal products were thiodi-

PRODUCTS FORMED BY THE ACTION OF SULFUR ON ANILINE



phenylamine (X) and phenyldiaminophenyl disulfide (IX). He showed that the thiodiphenylamine (X) was formed by the splitting off of the mercaptan and the closing of the ring.

Hodgson[21] has recently studied the action of sulfur on aniline and has shown how many of the seemingly discordant results obtained by the different workers could be reproduced. He found that the initial product of the action of sulfur on aniline at 170–180° is 2 : 2′-diaminodiphenyl disulfide (I), but increasing quantities of 4 : 4′-diaminodiphenyl disulfide (II) were formed with rising temperature. On prolonged heating and with excess of aniline, the disulfides underwent transformation into 2 : 2′-diaminodiphenyl sulfide (III), 2 : 4′-diaminodiphenyl sulfide (IV), and 4 : 4′-diaminodiphenyl sulfide (V). On heating with excess of sulfur, by diphenylamine condensation and further sulfuration, a substance $C_{18}H_{14}N_2S_3$ was produced, to which the structure (VII) was assigned, together with its desulfuration product, $C_{13}H_{14}N_2S_2$ (VIII). Merz and Weith's thioaniline[2] from sulfur and boiling aniline was found to be 2 : 4′-diaminodiphenyl sulfide (IV) with a little 4 : 4′-diaminodiphenyl sulfide (V). In the presence of litharge, he obtained the latter sulfide, thus showing that litharge promotes para substitution.

Also Hodgson[16] prepared trithio-*o*-toluidine by heating sulfur, *o*-toluidine, and *o*-toluidine hydrochloride at 180–190°, in almost quantitative yield. Later,[17] in the same manner he prepared trithioaniline from aniline in almost as good yield as the above. Previous to this work he took out a patent covering use of these bases as dyes.[15] The patent states, "Aniline and *o*-toluidine yield trithio compounds, while *m*- and *p*-toluidine give dithio compounds. Diazo dyes are obtained by combining the tetrazo compounds of the above described thio bases with naphthol or aminonaphthol sulfonic acids, or both." Gatterman prepared dehydrothio-*p*-toluidine and dehydrothio-*o*-toluidine[5] by heating *p*-toluidine and *o*-toluidine respectively with sulfur for 18 hours at 180–190°.

In a way similar to the preparation of thioaniline, Merz and Weith[2] obtained thio-*p*-toluidine from *p*-toluidine. Bogert and Mandelbaum[18] have recently investigated the latter reaction

and succeeded in isolating a dithio-*p*-toluidine from the resinous by-products. The latter workers also showed the sulfur linking of thio-*p*-toluidine to be ortho to the amino groups, by eliminating the latter through the diazo reaction and oxidizing the sulfide obtained to *mm'*-ditolylsulfone. This sulfone was synthesized by heating *m*-iodotoluene and sodium-*m*-thiocresylate in the presence of copper powder, and oxidizing the resultant sulfide. Truhlar[3] described a number of derivatives of thio-*p*-toluidine prepared by condensing the amino groups with various reagents. He attempted unsuccessfully to replace the amino groups with halogen or cyanogen by means of the Sandmeyer reaction, but succeeded in forming, by the diazo reaction, the corresponding phenolic compound.

Discussion

The reaction was carried out according to the directions of Bogert and Mandelbaum, with the exception that a lower temperature (130–140° instead of 140–145°) was used. Sulfur and *p*-toluidine were melted together in the proportions called for by the equation,

$$2CH_3C_6H_4NH_2+2S+PbO\longrightarrow(CH_3C_6H_3NH_2)_2S+PbS+H_2O.$$

When the temperature of the fusion mixture had reached 130°, litharge was added slowly to the well stirred mixture. Each fusion required from $7\frac{1}{2}$ to 8 hours.

It was found early in the work that the method of separation of the fusion products developed by Bogert and Mandelbaum, although much better than any heretofore used, was very troublesome to carry out and involved the use of comparatively expensive materials. The tars formed during certain stages of the extraction made the separation difficult to carry out. The method of the above workers was based on the difference in the basicities of the fusion products, and consisted in extracting their solution in benzene with a series of weak acids, each somewhat stronger than the antecedent one. An advantage of this method over previous ones was that thio-*p*-toluidine of a high purity was obtained.

It appeared to us that if the major products of the fusion were of different basicity, as they had been shown to be, they

could be wholly separated by fractional neutralization. That is, by dissolving the fusion products in an acid solution and slowly adding ammonia. This would eliminate the use of organic solvents and make the separation easier to handle. The important point was to find some way of recognizing the end point at that concentration of acid, where all of one substance had been precipitated and could be separated from the solution before any of the substance of next greater basicity began to precipitate. It was found that by stirring and slowly adding ammonia to an acid solution of the fusion products, all of the disulfide would be precipitated as a tarry solid before any thio-*p*-toluidine appeared as a crystalline precipitate. Further addition of ammonia to the filtrate until the odor of *p*-toluidine became apparent precipitated the thio-*p*-toluidine, and neutralization of the filtrate gave *p*-toluidine.

Instead of extracting the melt with alcohol, evaporating off the alcohol and then dissolving in dilute hydrochloric acid as previous investigators had done, it worked just as well to extract the melt directly with 10% acid. Four extractions of 800 cc. each were found to be the optimum number for obtaining the fusion products. Further extractions yielded but little additional solids, while fewer extractions entailed considerable loss. After each extraction the liquid was filtered, poured into water, and the resulting precipitate filtered off. This precipitate consisted of the acid soluble resins, very little dehydrothio-*p*-toluidine, and some inorganic salts.

On account of the large volume of solution obtained when the extracts were poured into water, the most convenient way of handling them was to add ammonia to the solution obtained from each extract until the odor of *p*-toluidine was apparent, filtering off the mixture of mono- and disulfide, and then neutralizing the solution to give the *p*-toluidine. The crude mono- and disulfide from the different extractions were then united, and redissolved in a much smaller volume of acid, the separation being carried out as given.

Summing up, in this method of fractional precipitation, the products are separated in the order of increasing basicity. First those whose salts are hydrolyzed by water are precipitated,

then in order appear dithio-*p*-toluidine, thio-*p*-toluidine, and finally *p*-toluidine.

In this research it was our purpose to find out how the yields of thio-*p*-toluidine, dithio-*p*-toluidine, and any other products of the reaction, varied with different temperatures and different concentrations of starting materials. Dehydrothio-*p*-toluidine, isolated during the course of the work, occurred in such small amounts (less than 1%) that it was useless to try to find changes in its concentration for each fusion. All of the products of the reaction have not as yet been identified. An acid soluble portion of these unidentified products can be separated rather easily from the other fusion products, and the yields followed under different conditions. Considerable time was spent in trying to isolate new compounds from this mixture. For the sake of clearness and in order to give these acid soluble products a name, we will call them the fusion residue throughout this dissertation.

In trying to increase the yield of the disulfide a large excess of sulfur was used. Also the concentration of the *p*-toluidine was kept low by grinding it with the litharge and then adding this mixture slowly. When five times the molar proportion of sulfur was used, the yields of thio-*p*-toluidine, the disulfide, and the recovered *p*-toluidine were very small, while the yield of fusion residue correspondingly increased. In the same way a fusion carried out using a mole and a half of sulfur gave a large yield of the fusion residue and a small one of disulfide. Bogert and Mandelbaum also found that an excess of sulfur decreased the yield of thio-*p*-toluidine (on basis of the recovered *p*-toluidine).

Since the presence of an excess of sulfur decreased the yield of thio-*p*-toluidine, it was thought that adding the sulfur slowly and thus keeping its concentration low would increase the yield. This is the reverse of the above process in that the sulfur was added with the litharge. The yields of thio-*p*-toluidine were appreciably increased while the amounts of unchanged *p*-toluidine were very large. When one and one half times the molar proportion of sulfur was added in the same way, it gave about the same yields of products as when molar

proportions of sulfur and *p*-toluidine were initially heated together. Three times the amount of sulfur did not seem to change these yields when added as given. That is, the favorable effect of adding the sulfur slowly seemed to be balanced by the unfavorable one of having an excess of sulfur.

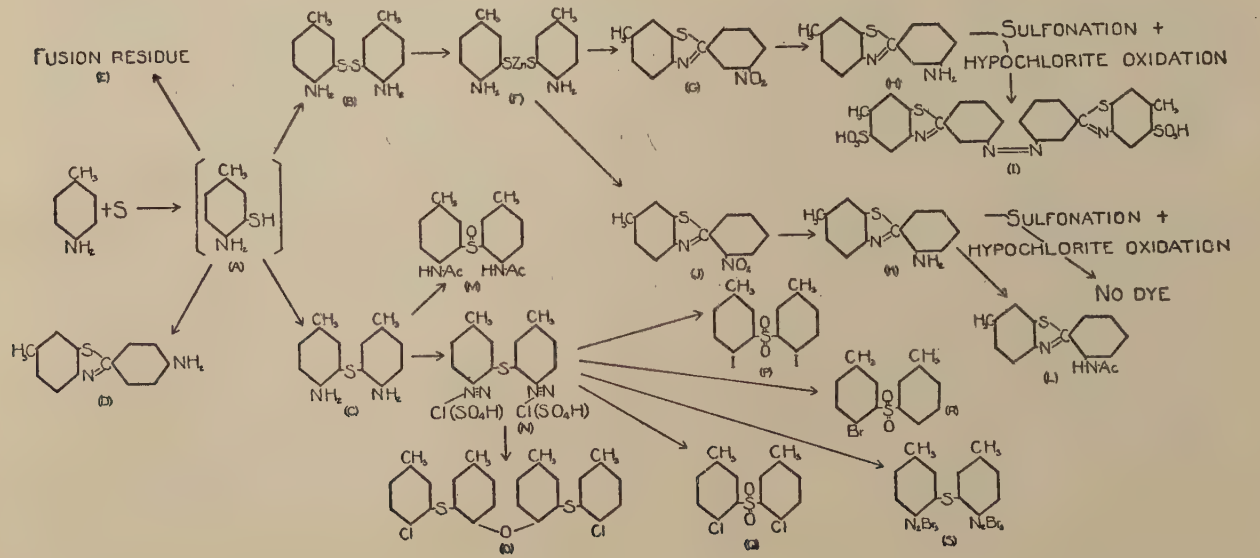
The above fusions were carried out at the temperatures used by Bogert and Mandelbaum, *i. e.*, 140–145°. Fusions carried out at higher temperatures (165°) gave smaller yields of the mono- and disulfides, and larger amounts of the fusion residue. It was found that if the fusion was carried out at a lower temperature (130–140°), the yield of the disulfide was increased and that of fusion residue decreased, while the amounts of thio-*p*-toluidine formed and the *p*-toluidine recovered were not appreciably changed.

All the above results are the averages of a large number of fusions. Sometimes the yields varied more under the same conditions than they did when the fusion was carried out under different conditions.

At 140–145°, Bogert and Mandelbaum reported the yield of thio-*p*-toluidine at around 30%, and that of the disulfide at less than 5%. Our experience with the fusions carried out at the same temperature and conditions, was that the yield of the disulfide differed, being over 10%. However, we separated the products in a different way, namely, by fractional neutralization and this fact may account for the difference in yields. It is very probable that the tars which separated in certain stages of the extraction, as carried out by Bogert and Mandelbaum, contained considerable amounts of disulfide.

At 130–140°, the yields of thio-*p*-toluidine were from 25–30%, while that of the disulfide varied from 15–20%. The amount of the fusion residue extracted was never equivalent to more than 20% of the *p*-toluidine, and maybe much less. Thus, at least 30% of the *p*-toluidine used is unaccounted for. The loss is probably due in part to each of the following: (1) Incomplete extraction. (2) Oxidation and charring of the amines in the presence of sulfur and litharge. (3) Steam distillation of *p*-toluidine in the presence of the water formed during the fusion.

FLOW SHEET


FUSION RESIDUE
(E)
+S
(A)
(B)
(F)
(G)
(H)
—SULFONATION +
HYPOCHLORITE OXIDATION
(I)
(J)
(K)
—SULFONATION +
HYPOCHLORITE OXIDATION
NO DYE
(L)
(M)
(C)
(N)
(D)
(O)
(P)
(Q)
(R)
(S)

The results obtained by Hodgson[21] on the reaction of sulfur on aniline, would tend to show that a disulfide is first formed, and this in turn, in the presence of excess aniline and litharge, is converted into a monosulfide. He obtains almost the calculated yield of monosulfide by heating the disulfide with excess aniline and litharge. Hoffman[8] also obtained thioaniline (V) by heating the disulfide (I) with litharge in the presence of aniline. Similarly, we hoped to convert dithio-*p*-toluidine (B) into thio-*p*-toluidine (C) and show the course of the reaction to be the same as in the case of aniline. But when dithio-*p*-toluidine was heated with excess *p*-toluidine and litharge, we recovered most of our starting materials unchanged and were unable to find any trace of thio-*p*-toluidine, even though Hodgson obtained the corresponding monosulfide in almost the calculated yield. According to these results, it does not seem likely to us that the reaction of sulfur on *p*-toluidine takes place in the same manner as that of sulfur on aniline. Further evidence that the action of sulfur on aniline is not the same as that of sulfur on *p*-toluidine, is the different products formed in the presence of hydrochloric acid, under the same conditions.

It has been suggested by Bogert and Mandelbaum that the course of the reaction is, in the presence of litharge at a temperature of 140–145°, through the mercaptan (A). This, by the simultaneous oxidizing influence of the sulfur and litharge, unites with the unchanged *p*-toluidine to form thio-*p*-toluidine (C), while small amounts escape this reaction, and are oxidized to the disulfide (B). In the absence of litharge, and at the higher temperature employed (180–220°) for the manufacture of dehydrothio-*p*-toluidine and primuline, the mercaptan condenses with the methyl group of unchanged *p*-toluidine, thus generating a compound which is more stable than thio-*p*-toluidine under these conditions of temperature. This latter theory, which seems to be the most probable by which dehydrothio-*p*-toluidine (D) is formed from *p*-toluidine and sulfur, is generally accredited to Friedländer[11]. But it was found the Ziegler[6] had made this deduction 15 years before Friedländer had published his theory.

In the former lower temperature reaction, Bogert and Mandelbaum also pointed out that it seemed likely that the thio-*p*-toluidine formed reacted with the sulfur, the reaction becoming as great at certain concentrations of sulfur, as the velocity of formation of thio-*p*-toluidine itself. In support of this assumption, they found that an increase in the amount of sulfur used in the reaction resulted in no increase in the amount of thio-*p*-toluidine, but a decrease in the weight of *p*-toluidine recovered and the formation of more tarry by-products. Similarly, any considerable prolongation of the heating after the requisite amount of litharge had been added tended to diminish the yield.

In order to test out this latter assumption, determine the extent of the reaction, and find out if any fusion residue was formed, thio-*p*-toluidine, sulfur, and litharge were fused together, in the absence of *p*-toluidine, under the same conditions as the reaction is ordinarily carried out. When extracted with acid the fusion mixture yielded 84.5% of the original thio-*p*-toluidine, and only a trace of the fusion residue. Since there was no *p*-toluidine present, the concentration of both the sulfur and thio-*p*-toluidine were very much greater than any concentration both substances could attain during a fusion as ordinarily carried out. Also, on account of the larger proportion of sulfur and litharge, in the absence of *p*-toluidine as a solvent, we must expect more oxidation and charring of thio-*p*-toluidine through attacking the amino groups. Thus, it does not seem likely that thio-*p*-toluidine reacts to any great extent with sulfur under the same conditions as the reaction is ordinarily carried out. At least, in the light of the experimental results obtained above, such a reaction would not account for the greatly lowered yields of thio-*p*-toluidine that were observed when excess sulfur was present.

In order to find out whether the disulfide reacted with sulfur, or sulfur and litharge, to form the fusion residue, it was heated with litharge and sulfur for eight hours at a comparatively high temperature. Some fusion residue (acid soluble resins) was obtained but most of the disulfide was recovered unchanged.

The most probable primary step in the action of sulfur on

p-toluidine, as Bogert and Mandelbaum have pointed out, is the formation of the mercaptan. If we assume that this mercaptan reacts with sulfur to form the fusion residue (E), we can account for the results obtained. Now according to this asumption there are at least four ways in which the mercaptan probably would react under the conditions of the reaction:

(1) In the presence of sulfur to condense with *p*-toluidine to give thio-*p*-toluidine (C).

(2) Oxidation by either litharge or sulfur to give the disulfide (B).

(3) With sulfur to give the fusion residue (E).

(4) With *p*-toluidine to give a small amount (less than 1%) of dehydrothio-*p*-toluidine (D).

According to our results, we can say that (1) takes place most readily with excess of *p*-toluidine and a temperature of 130–145°. It may be pointed out that the oxidizing agent in this condensation is very probably sulfur and not litharge. That is, sulfur reacts with the mercaptan and *p*-toluidine to give thio-*p*-toluidine and splitting off hydrogen sulfide, the latter then reacting with the litharge to give lead sulfide and water. This explanation is supported by the fact that Bogert and Mandelbaum obtained thio-*p*-toluidine by adding lead carbonate to a sulfur-toluidine mixture at 165–170°, thus showing that the presence of litharge was not essential. (2) Takes place best at a temperature of 130-140°, for we obtained our best yields of disulfide under these conditions. Excess of sulfur and higher temperatures favor (3) for the yield of fusion residue is always increased when excess sulfur is added, or when the temperature is increased, with a corresponding decrease in the amounts of the other fusion products. (4) Takes place best the higher temperature above 140° (within certain limits).

The fact that we obtained some fusion residue (acid soluble resins) when thio- and dithio-*p*-toluidine were heated with sulfur and litharge, can be accounted for by assuming that they dissociated or decomposed into the mercaptan, and this reacted with the sulfur as already stated. The sulfur to sulfur

linking in the disulfide being comparatively weak, we would expect more decomposition in the case of the disulfide than in the case of thio-*p*-toluidine. The amounts of fusion residue formed when thio- and dithio-*p*-toluidine were heated with sulfur and litharge in the above experiments, bear out this supposition.

A number of derivatives of thio-*p*-toluidine were prepared by replacing the amino groups by halogens. Truhlar[3] mentions the fact that he had tried to make the dichlor-, dibrom- and dicyan- derivatives by replacing the amino groups by means of the Sandmeyer reaction, with the result that he obtained dark viscous tars. Repeating Truhlar's work, we also found these tars, out of which no crystalline product could be obtained. Oxidation of these tarry products to the sulfones, with a mixture of concentrated nitric and sulfuric acids, produced solids, and although we were unable to crystallize them, they were in better form to be purified. All of these sulfones decomposed slowly at temperatures below 100°. Analyses showed that replacement of the amino groups by the halogen had taken place.

The Gatterman reaction followed by oxidation, was found to give the best yield of the chlorine compound (Q). In the case of the bromine compound (R), our analyses showed that only one of the amino groups had been replaced by a bromine atom, the other being replaced by a hydrogen. Potassium iodide, when added to the diazochloride (N), produced a tarry compound which on oxidation gave the di-iodo sulfone (P) in good yield. We attempted to prepare the dicyan derivative by means of the Sandmeyer reaction, and then hydrolyze this to the acid, but the yield of acid was so poor that no further work was attempted.

An unusual replacement of the diazonium compound occurred, and according to our analyses, a complex ether (O) formed, when the diazochloride (N) was treated with concentrated hydrochloric acid. Truhlar mentions the formation of an "easily frozen, chlorine containing oil," by heating the diazochloride with excess concentrated hydrochloric acid, but he was unable to identify it. Aromatic ethers can be prepared

from diazonium salts by heating them with phenols, so it is probable in this reaction that ether formation occurrs in the same manner, that is, one diazo group of some of the dis-diazonium salt is replaced by an OH group to form a phenol, and this phenol in turn reacts with an unchanged diazo group of another molecule to form an ether; the remaining diazo groups on the molecule being replaced by chlorine in the usual manner.

The perbromide (S) was easily prepared by adding bromine to the diazonium solution. We attempted to make the azide by treating the perbromide with concentrated ammonium hydroxide, but were unable to get a crystalline derivative from the reaction products. On boiling the perbromide with alcohol, we obtained a small yield of an oil which was not oxidized to a solid sulfone with concentrated nitric acid. This suggests that the oil may have the same kind of structure as the chlor ether.

A sulfoxide (M) was prepared by oxidizing the acetyl derivative of thio-*p*-toluidine with hydrogen peroxide in glacial acetic acid solution.

With the aid of a new synthesis which has just been developed,[19,20] we prepared nitrobenzothiazoles from dithio-*p*-toluidine. The disulfide (B) was dissolved in glacial acetic acid and boiled with an excess of zinc dust. Filtration of the hot acetic acid solution, after reduction, into several volumes of water precipitated the zinc salt (F). This when fused with *m*-nitrobenzoyl chloride gave *m*-nitrophenyl benzothiazole (G). The fusion of the zinc salt with *o*-nitrobenzoyl chloride was carried out in glacial acetic acid solution, giving the corresponding *o*-nitrophenyl benzothiazole (J). The two nitrobenzothiazoles thus obtained were reduced to the amino compounds in the usual way with tin and hydrochloric acid.

Columbia Yellow or Chloramine Yellow, a yellow dye obtained by alkaline oxidation of dehydrothio-*p*-toluidine sulfonic acid with hypochlorite, has recently been shown to have an azo structure.[20] It is an extremely fast dye on cotton, and important commercially. We hoped that by similar oxidation of the ortho and meta isomers of dehydrothio-*p*-toluidine

sulfonic acid, we could show the effect of different positions of the amino group on the dye, or suggest modifications to change the shade and yet retain the color fastness.

The aminobenzothiazoles obtained above were sulfonated according to the method of Green.[4] In preparing the dyes we used the hypochlorite method described in the German patent[7] for making Columbia Yellow from the monosulfonate of dehydrothio-*p*-toluidine. From the meta compound (H), there was obtained a yellow dye of much lighter shade than Columbia Yellow, which we think has the structure (I), fast to cotton, and otherwise of similar properties. However, we were unable to obtain a similar dye from the ortho isomer (K). The dyes prepared from the para and meta compounds, both gave deep carmine red solutions with concentrated sulfuric acid, while the corresponding product obtained by sulfonation and oxidation of the *o*-aminobenzothiazole gave the solution only a light reddish brown tinge. This reaction seems to be a test for the azo structure, and leads us to believe that oxidation of the ortho isomer did not take place. Further, the sulfonic acid group may not have entered the same position as in the other isomers. The product obtained by sulfonation was not similar in form to that obtained from the meta and para compounds.

Experimental Part

The fusion and the separation of the products.

The fusion was carried out according to the directions of Bogert and Mandelbaum, with the exception that a slightly lower temperature was used. Five hundred and thirty-five g. of *p*-toluidine, 160 g. of sulfur, and 800 g. of litharge were conveniently fused together in a 2 l. flask. When the temperature of the melt had reached 130°, litharge was added to the well stirred mixture through a period of six hours, finally heating for another $1^1/_2$–2 hours after all the litharge had been added. The temperature was kept between 130–140°, never letting it rise above the latter.

The flask was transferred from a paraffin to a sand bath, and extracted with 800 cc. portions of 10% HCl (by weight). When much stronger acid was used the copious evolution of hydrogen sulfide caused the solution to boil over the flask. The mixture was heated to boiling for five minutes and well stirred, the resulting solution being decanted into a suction filter. In order to find the optimum number of extractions necessary, each 800 cc. extract from a fusion was neutralized with ammonia,

and the precipitate filtered off and dried. The first three extractions gave 444 g. of solids, a fourth 56 g., a fifth 21 g. To find out how well the hydrochloric acid had extracted the fusion mixture compared to alcohol, and also to take out any products which might be insoluble in the hydrochloric acid, the residue was boiled with 1/2 l. of alcohol. On evaporating off the alcohol and drying only 10 g. of solids were obtained. Total solids 531 g. or 86% of the total weight of the initial *p*-toluidine plus 1/2 the sulfur.

In carrying out the separation, each 800 cc. extract was filtered and poured into water. The yellow amorphous solid (the fusion residue) that precipitated, was filtered from the solution. Conc. NH_4OH was added slowly with stirring to the solution, until the odor of *p*-toluidine became apparent. The precipitate formed, consisting of the disulfide and thio-*p*-toluidine, was filtered off. Neutralization of the filtrate gave *p*-toluidine which did not need any further purification.

The precipitates from the different extractions were united and dissolved in 1.8 l. of boiling 10% HCl. Conc. NH_4OH was then added as before, to precipitate the disulfide. The color of the precipitate changed from yellow to pink to red as the addition of ammonia was continued. The solution should be slightly warm (30–50°), in order to insure the precipitation of the disulfide in the easily recognizable tarry form. As much of the disulfide as possible was removed from the solution as soon as it precipitated, by means of a stirring rod. When most of the disulfide had been precipitated, the solution was stirred vigorously and the ammonia added very slowly. Finally the precipitate changed from a tarry character to a crystalline one. The precipitate, consisting of the remaining disulfide and some thio-*p*-toluidine, was filtered off at once. There was not enough of it to rework, so it was discarded. Ammonia was added to the filtrate until the odor of *p*-toluidine became apparent, or if there was no *p*-toluidine, until the solution was neutralized. The crude thio-*p*-toluidine was filtered from the solution.

The tarry disulfide from the above was dissolved in boiling 10% HCl, and then poured into an equal volume of water. Any fusion residue present was precipitated and filtered off, and the filtrate tested for more of the fusion residue by adding cold water. Then ammonia was added to the warm solution, as in the first part of the separation, until a crystalline precipitate appeared. The small amount of thio-*p*-toluidine separated was combined with the rest from the previous separation.

The crude thio-*p*-toluidine was dissolved in hot 10% HCl, and the separation given before was repeated. If there happened to be any disulfide present it was precipitated first, while any *p*-toluidine precipitated last. By repeating this process thio-*p*-toluidine of any desired purity could be obtained. If thio-*p*-toluidine of an exceptional high purity was desired, it was more convenient to take the crude product obtained here and revert to the purification given below, rather than to make many fractional neutralizations.

A typical fusion, using four extractions of 10% HCl, gave the following yields of crude products: 167 g. of recovered *p*-toluidine, 70 g. of fusion residue, 80 g. or 17% by theory of disulfide (based on the recovered *p*-toluidine), and 26% by theory of thio-*p*-toluidine.

A separation was carried out using 10% sulfuric acid (by weight) instead of hydrochloric, and it worked just as well giving the same yields of products.

Purification of thio-p-toluidine.

The thio-*p*-toluidine obtained above is only slightly colored, and melts over 100°. It is further purified by dissolving in 10% HCl and adding conc. HCl until precipitation commences, as recommended by Bogert and Mandelbaum. By itself, the precipitation of the hydrochloride is not a good method of purification, for the hydrochloride of dithio-*p*-toluidine precipitates almost as well. The hydrochloride is then dissolved in boiling water and the solution neutralized with ammonia. Some thio- and dithio-*p*-toluidine can be recovered from the mother liquor of the hydrochloride by carrying out a fractional neutralization with ammonia. The thio-*p*-toluidine is finally recrystallized once from dilute alcohol, giving colorless leaves, m. p. 103–104°.

Purification of dithio-p-toluidine.

The tarry disulfide when dried varied from a light yellow to a deep red. However, the color was not found to be an indicator of purity. The crude product was purified by dissolving in hot alcohol and adding water until an oil separated. The solution was then let stand until the disulfide crystallized. The addition of conc. ammonia instead of water seemed to help crystallization in certain cases.

Separation of dehydrothio-p-toluidine from the fusion products.

The yellow fusion residue was boiled with a large volume of distilled water in order to rid it of any soluble organic or inorganic compounds. The hot solution was separated from the melted fusion residue, filtered, and a cloudy solution obtained. After several extractions a clear solution was obtained. The latter solution was fluorescent, but on cooling it lost this fluorescence and deposited a white flocculent precipitate. In alcohol this precipitate was deeply fluorescent and melted at 186°, indicating it to be dehydrothio-*p*-toluidine. No fluorescence could be noticed in an alcoholic solution of the original yellow fusion residue, the dark color of the solution effectively hiding it. However, when the latter solution was placed under ultra-violet light, the liquid on the sides of the glass vessel fluoresced strongly. After repeated extractions with large volumes of hot water, 20 g. of fusion residue, obtained from a fusion carried out at 140–145°, gave 0.96 g. of dehydrothio-*p*-toluidine, or much less than 1% of the theory based on the original fusion. The fusion residue obtained from fusions carried out at 130–140°, gave only traces of dehydrothio-*p*-toluidine.

Further investigation of the fusion products.

A part of the residue after the above water extraction was boiled with a large volume of alcohol to dissolve as much of it as possible, then filtered. After several extractions the residue contained mostly inorganic salts. When water was added to the alcoholic solution, it precipitated a dark mass, which became a greenish brown on drying. This brown precipitate when dissolved in concentrated hydrochloric acid, in which it is slightly soluble, and poured into water, formed a bright yellow flocculent precipitate. This yellow substance is evidently the same as that observed by Bogert and Mandelbaum, who extracted the sulfuric acid insoluble portions of the fusion products with concentrated hydrochloric acid and then poured the solution into water.

The fusion residue is soluble in hot alcohol, acetone, or benzene, and when small amounts of these solvents come in contact with the solid the whole mass becomes tarry. Easily soluble in glacial acetic acid, and dissolves readily in acetic anhydride with a large evolution of heat. Attempts to crystallize the acetyl, benzoyl, and picrate derivatives failed. It is insoluble in cold dilute acids, but somewhat soluble hot. Melts with some decomposition at 60–80°. On long boiling with tin and hydrochloric acid, hydrogen sulfide was slowly evolved, but at the end of six hours very little had gone into solution, leaving a resinous substance. From the solubilities and other properties, it would seem as if the nitrogen were bound up in some sort of a ring structure.

For analyses the solid was precipitated from alcohol and acetone solutions by adding water, then dissolving in hot concentrated hydrochloric acid and pouring into water, finally washing with water. Analyses on samples from different fusions carried out under the same conditions varied widely. From these analyses we were unable to get a clue to the probable structure, so further work was thought unprofitable. We were unable to isolate any trisulfide or sulfone from the fusion residue.

Attempt to isolate an indicator present in the fusion products.

When the disulfide from the fusion is precipitated from an acid solution by an alkali, the color of the precipitate changes from a yellow to a pink, and finally to a deep red. It was found that if the yellow part of the precipitate, which is taken off before it changes color to a pink, is dissolved in acid and reprecipitated, it shows only a slight color change. This would tend to show that most of the indicator remains in solution until that concentration where the pink changes to red. Twenty-five grams of the disulfide was repeatedly dissolved and reprecipitated from an acid solution, each time the yellow part of the precipitate being removed. In this way it was worked down to about 2 grams, and the tarry solid dried. This was acetylated, and it was found that there was not enough of the indicator present to noticeably affect the yield or the melting point of the acetylated disulfide formed. Bogert and Mandelbaum were also unable to isolate the indicator.

The fusion of sulfur with p-toluidine in the presence of hydrochloric acid.

Hodgson[16] prepared trithio-*o*-toluidine in quantitative yield by heating 100 g. of *o*-toluidine, 50 g. of *o*-toluidine hydrochloride, and 50 g. of sulfur at 185–190° for 2–3 hours. A quantitative yield of trithioaniline was obtained under the same conditions.[17] He states that the equivalent of hydrochloric acid and the base can be used in place of the hydrochloride. We prepared trithio-*o*-toluidine according to Hodgson's directions, using hydrochloric acid. The hydrochloride of the base was obtained in good yield and after two recrystallizations from hot dilute HCl, the product melted at 225° uncor., compared to 226–227° uncor., reported for the m. p. of trithio-*o*-toluidine hydrochloride.

Hodgson mentions in his patent[15] that under the above conditions *p*-toluidine gives the dithio compound. We heated 35 g. of *p*-toluidine, 10 cc. of conc. HCl, and 12½ g. of sulfur (same proportions as those used for *o*-toluidine) for 2 hours at 185–190°. A short neck flask was used and the water present distilled off at once. The fusion mixture was extracted with 10% HCl, the extract filtered, and when fractionally neutralized gave 6 g. of *p*-toluidine. Also there was obtained 4 g. of a deep red tarry substance, resembling in form the disulfide obtained in other parts of this work by the fusion of sulfur with *p*-toluidine in the presence of litharge. The acetyl derivative of this base was prepared, and after many recrystallizations from diluted alcohol, by which the yield is reduced almost to nothing, a m. p. of 209° corr. was obtained, showing this base to be dithio-*p*-toluidine. The rest of the fusion mixture, consisting of nearly 90% of the whole, was a black mass insoluble in conc. HCl and alcohol. No trace of the fusion residue, obtained in other parts of this work, was found when this black mass was extracted with boiling conc. HCl and the extract poured into water.

A fusion carried out for three hours instead of two gave a much less recovery of *p*-toluidine, more of the insoluble residue, without changing the yield of the disulfide.

The poor quality and low yield of the disulfide obtained from the fusion of sulfur and *p*-toluidine in the presence of hydrochloric acid, contrasted sharply with the purity and good yields of the trithio product obtained from the fusion of sulfur and *o*-toluidine under the same conditions.

Properties of thio-p-toluidine not reported in the literature.

Thio-*p*-toluidine is a very stable configuration. Acetylated it resists ordinary nitration, bromination, and sulfonation; while more strenuous application of these reagents decomposes the molecule, probably through attacking the amino group. Treatment of acetylated thio-*p*-toluidine with a 7.5 : 3 mixture of nitric and sulfuric acids at room temperature was found to be a convenient way of preparing the sulfone. Although it readily diazotizes and couples with amines and phenols, thio-*p*-toluidine would not couple with diazotized sulfanilic acid in acid solution, *i. e.*, it would not act as a secondary coupling agent. Methylation with the use of

methyl sulfate at ordinary temperatures in both water and ether solution produced tars, out of which we are unable to get a crystalline derivative.

Attempts were made to form the corresponding thiazine compound by eliminating an amino group and closing up the ring. Heating with such condensing agents as soda lime and zinc chloride failed. Employment of the same conditions as in the formation of ditolylamine from *p*-toluidine, *i. e.*, by heating with hydrochloric acid under pressure, did not yield any results. By using concentrated hydrochloric acid and heating for a longer time at a higher temperature (200°), we were able to decompose the molecule of thio-*p*-toluidine into *p*-toluidine, without producing any trace of the corresponding thiazine compound. The use of iodine and ferric chloride as catalysts under similar conditions did not change these results.

On heating thio-*p*-toluidine, it begins to decompose around 200°. At 230° ammonia is given off. Further heating completely decomposes the thio-*p*-toluidine giving off a pungent disagreeable vapor.

The following experiment was carried out to determine the extent of reaction between thio-*p*-toluidine, sulfur, and litharge. Seventy-one g. of carefully purified thio-*p*-toluidine (m. p. 103–104°), were heated with 19 g. of sulfur at 140–150°, and 65 g. of litharge added during the course of 8 hours. When extracted with hydrochloric acid the fusion mixture yielded 60 g. of thio-*p*-toluidine or 84.5% of the amount started with, and only a trace of the fusion residue.

Bis[2(2'-chlor-5'-methylphenyl sulfide)-4-methylphenyl] oxide.

Twenty-four and five tenths g. of thio-*p*-toluidine were dissolved in 100 cc. of conc. HCl and 150 cc. of water. The hydrochloride precipitated at once in the cold. The mixture was cooled to 0°, and 15 g. of sodium nitrite added in 75 cc. of water. After standing a half hour, the solution was poured into 450 cc. of conc. HCl and left over night at room temperature. Gas was slowly evolved. It was heated gradually to boiling when an oil began to separate. In a short time the reaction was at an end. The black oil was separated from the solution, and washed with strong alkali and water. When distilled in vacuo it boiled at approximately 265° under 80 mm. pressure, giving a colorless, light, viscous oil. Yield 15 g. or 59%.

Combustion analysis.

Sample—0.1280 g. Water—0.0580 g. CO_2—0.3082 g.
Calc. for $C_{28}H_{24}OCl_2S_2$: C—65.75%, H—4.69%.
Found: C—65.66%, H—5.07%.

The Carius method was used for determining sulfur and chlorine.

Sample—0.2041 g. $BaSO_4$—0.1904 g.
—0.2164 g. AgCl—0.1261 g.
Calc. for $C_{28}H_{24}OCl_2S_2$: S—12.52%, Cl—13.90%.
Found: S—12.81%, Cl—14.42%.

A distinctive and striking property is the deep blue color this ether gives with conc. sulfuric acid. Oxidation with acid permanganate did not form a solid sulfone, while strong oxidation with conc. nitric acid decomposed the molecule.

Bis(2-iodo-5-methylphenyl) sulfone.

Five g. of thio-*p*-toluidine were dissolved in 80 cc. of water and 12 cc. of conc. HCl. Ice was added and the solution diazotized in the usual way with a solution of 3.3 g. of sodium nitrite, the temperature being kept below 10°. A cold concentrated solution of 12 g. of potassium iodide was then slowly run in with continuous stirring. At first rapid evolution of nitrogen took place, but towards the end of the reaction, became less vigorous and had to be assisted by warming on the water bath. When no more nitrogen was evolved, the black viscous mass was collected and washed with water. It was dissolved in glacial acetic acid and enough potassium bisulfite added so that there was no evolution of iodine when the acetic acid solution was boiled. When poured into water it gave a yellow gummy substance. Small portions were then added to a mixture of 15 cc. of nitric acid and 6 cc. of conc. sulfuric acid. The mixture was warmed until there was a copious evolution of nitrogen dioxide, when the reaction was over almost at once. The acid mixture was poured into water and a solid obtained. This solid was warmed with strong NaOH, removed and dissolved in boiling glacial acetic acid, boneblacked, poured into water, and the precipitate washed with hot alcohol. Attempts to crystallize it failed, so it was again dissolved in glacial acitic acid, boneblacked, poured into water, washed and dried, giving a light brown product. Yield 4.3 g. or 42%. It is readily soluble in chloroform, acetone, and carbon disulfide; soluble in benzene; slightly soluble in ether; insoluble in alcohol and carbon tetrachloride.

Combustion analysis.

Sample—0.2095 g. Water—0.0422 g. CO_2—0.2546 g.
Calc. for $C_{14}H_{12}O_2I_2S$: C—33.73%, H—2.43%
Found: C—33.14%, H—2.25%

The Carius method was used for determining sulfur and iodine.

Sample—0.1909 g. $BaSO_4$—0.0875 g.
—0.1898 g. AgI—0.1764 g.
Calc. for $C_{14}H_{12}O_2I_2S$: S—6.44%, I—50.96%
Found S—6.30%, I—50.25%

Bis(2-chlor-5-methylphenyl)sulfone.

Five g. of thio-*p*-toluidine were dissolved in 80 cc. of water and 12 cc. of conc. HCl. Ice was added and the solution diazotized with a solution of 3.3 g. of sodium nitrite. Six g. of copper powder was added and the whole allowed to stand an hour, finally heating on the water bath until no more nitrogen was evolved. The tarry precipitate formed was

separated from the liquid, and oxidized as already given for the iodo compound. The nitric acid mixture was poured into water and let stand until the tarry mass solidified. It was dissolved in glacial acetic acid, boneblacked, washed with NaOH, hot alcohol, and water, giving a light brown amorphous product. Readily soluble in acetone, chloroform; soluble in benzene; slightly soluble in ether, carbon disulfide, and carbon tetrachloride; quite insoluble in alcohol. Yield 2.1 g. or 33%.

Combustion analysis.

Sample—0.1256 g. Water—0.0388 g. CO_2—0.2483 g.
Calc. for $C_{14}H_{12}O_2Cl_2S$: C—53.32%, H—3.84%
Found: C—53.91%, H—3.46%

2-Brom-bis(5-methylphenyl)sulfone.

The reaction was carried out under the same conditions as in the preparation of the chlorine compound. Ice was added to 17 g. of conc. sulfuric acid until the temperature falls to 0°. Five g. of thio-*p*-toluidine were added, and the solution diazotized with 3.3 g. of sodium nitrite. Thirty g. of potassium bromide and 10 g. of copper powder were then added, and after letting stand and heating, the product was separated, oxidized and washed as before giving a brown amorphous solid. Yield 3.6 g. or 54%. Readily soluble in benzene, chloroform, and acetone; quite soluble in ether; slightly soluble in carbon tetrachloride; insoluble in alcohol. Instead of the two amino groups being replaced by two bromine atom, our analyses showed that only one was replaced by a halogen, the other being replaced by a hydrogen.

Combustion analysis.

Sample—0.2160 g. Water 0.0703 g. CO_2—0.4131 g.
Calc. for $C_{14}H_{13}O_2BrS$: C—51.69%, H—4.00%
Found: C—52.16%, H—3.64%

Bis(2-diazo-perbromide 5-methylphenyl)sulfide.

Five g. of thio-*p*-toluidine were diazotized in the same manner as given for the bromine compound. Ten g. of bromine and 10 g. of KBr were dissolved in 10 cc. of water, and slowly added to the diazo solution. The perbromide precipitates at once as a red gum, insoluble in cold alcohol, ether, benzene, carbon disulfide, and carbon tetrachloride. It was collected, washed with water, and air dried. On account of its insolubility and instability, we were unable to obtain a sample sufficiently pure for analysis.

In order to prepare the bromine derivative from the diazoperbromide, the latter was boiled with alcohol, the residue filtered off, and the solution poured into a large volume of water. There was no precipitate, but when salt was added to the solution, a small yield of oil separated out. Oxidation of this oil with concentrated nitric acid did not give a solid sulfone.

Bis(2-acetamino-5-methylphenyl)sulfoxide.

We were unable to oxidize thio-*p*-toluidine with hydrogen peroxide in acetone solution according to the method of Gazdar and Smiles,[13] so Hinsberg's method[14] of oxidizing the acetyl derivative in acetic acid solution was used. Five g. of thio-*p*-toluidine were dissolved in 6 cc. of acetic anhydride. To this when cooled was added 20 cc. of glacial acetic acid and 2 cc. of 30% hydrogen peroxide (superoxole), and let stand 12 hours at room temperature. The acetic acid solution was poured into a large volume of water and neutralized with ammonia. On recrystallizing the precipitate from dilute alcohol, in which it was very soluble hot and quite soluble cold, it formed hexagonal colorless plates, m. p. 212° corr. Yield of pure product 2 g. or 28% of the theory.

Combustion analysis.

Sample—0.1709 g. Water—0.0899 g. CO_2—0.3935 g.
Calc. for $C_{18}H_{20}O_3N_2S$: C—62.75%, H—5.87%
Found: C—62.79%, H—5.89%

Properties of dithio-p-toluidine not reported in the literature.

Reduction of dithio-*p*-toluidine with zinc dust and acetic, and tin and hydrochloric acid, gave the zinc and tin salts of the mercaptan respectively. Detinning of these salts with hydrogen sulfide produced the free mercaptan, which was easily oxidized back to the disulfide by passing in air through its basic solution. Oxidation of acetylated dithio-*p*-toluidine with nitric acid, and also acid permanganate gave what appeared to be the corresponding sulfonic acid. We were unable to prepare the disulfoxide by oxidizing the disulfide with dilute hydrogen peroxide.

We attempted to convert dithio-*p*-toluidine into thio-*p*-toluidine as follows: 6 g. of dithio-*p*-toluidine, carefully purified from any thio-*p*-toluidine, were heated with 20 g. of *p*-toluidine at 140–150°, and during the course of the heating 10 g. of litharge were added. Five and one-tenth g. of the disulfide were recovered from the mixture, along with 18 g. of *p*-toluidine. No trace of thio-*p*-toluidine was found. Another fusion carried out at a higher temperature (160–165°), using the same proportions, also failed to give us a trace of the monosulfide.

For the purpose of finding out if there was any reaction between the disulfide, sulfur, and litharge to form the fusion residue, 9 g. of disulfide and 4 g. of sulfur were heated at 160–165° for eight hours, 10 g. of litharge being added during that time. From this fusion 0.7 g. of fusion residue were obtained, most of the *p*-toluidine and disulfide being recovered unchanged.

Zinc salt of 2-amino-5-methyl thiophenol.

Ten g. of crude dithio-*p*-toluidine were dissolved in 200 cc. of boiling glacial acetic acid, and 20 g. of zinc dust added. The whole was refluxed for one hour, filtered hot, and the filtrate diluted with 2.5 volumes of water. A white flocculent precipitate came to the surface. The solution was

allowed to stand 10–15 minutes in order to complete precipitation, but when allowed to stand a longer time an impure product was obtained. The precipitate was filtered, washed, and dried in the oven at 110°. If the solid softened in the oven it was washed with ether to remove the impurities. Longer boiling of the acetic acid solution than one hour decreased both the size and quality of the yield. Yield 5.6 g. or 45%.

Analysis. (The zinc salt was ignited to the oxide.)

Sample—0.9824 *g.* ZnO—0.2319 g.
Calc. for $C_{14}H_{16}N_2S_2Zn$: ZnO—23.82%
Found: ZnO—23.60%

2(m-Nitro phenyl) 6-methyl benzothiazole.

Three g. of the above zinc salt were ground up with 3.7 g. of *m*-nitrobenzoyl chloride in a mortar. The mixture was transferred to a test tube and heated on the boiling water bath for one hour, the viscous mass being stirred thoroughly. On cooling a hard cake was obtained. The cake was ground up and warmed with N NaOH for an hour. The remaining insoluble product was then recrystallized from glacial acetic acid, from which it was obtained in small yellow needles, m. p. 166° corr. It is insoluble in cold alcohol, moderately soluble hot; insoluble in ether, benzene, acetone; readily soluble in chloroform. Yield 1.4 g. or 58%.

Combustion analysis.

Sample—0.2066 g. Water—0.0743 g. CO_2—0.4702 g.
Calc. for $C_{14}H_{10}O_2N_2S$: C—62.22%, H—3.70%
Found: C—62.09%, H—4.02%

2(m-Amino phenyl) 6-methyl benzothiazole.

One and five-tenths g. of the above nitro compound were boiled with 5 cc. of conc. HCl, 95 cc. of water and 10 g. of granulated tin for two hours. The substance had all gone into solution at the end of one hour. The acid solution was made strongly alkaline with 4 N NaOH, and kept warm on the water bath for an hour. The insoluble product crystallized from alcohol in white needles, m. p. 181° corr. Yield 0.85 g. or 64%. It is readily soluble in alcohol, acetone, benzene, ether, and chloroform.

Combustion analysis.

Sample—0.1358 g. Water—0.0624 g. CO_2—0.3500 g.
Calc. for $C_{14}H_{12}N_2S$: C—70.00%, H—5.00%
Found: C—70.29%, H—5.14%

Sulfonation of 2(m-amino phenyl) 6-methyl benzothiazole.

The sulfonation was carried out under the same conditions as those used for making the monosulfonate of dehydrothio-*p*-toluidine.[4] Three-fourths g. of 2(*m*-amino phenyl) 6-methyl benzothiazole were dissolved in 5 cc. of conc. sulfuric acid and the solution cooled to 25°. Five cc. of fuming sulfuric acid (50% free SO_3) were then added slowly, never allowing the

temperature to rise above 50°. Heating was continued for 8 hours at 40–50°, after which, a drop of the sulfonation mixture tested with dilute ammonium hydroxide showed the sulfonation to be complete. When poured upon ice a flocculent yellow precipitate settled out and was filtered off. The product was purified by dissolving it in warm dilute alkali and precipitating with dilute sulfuric. Filtration and drying in the oven produced a dark brown solid. Yield 0.7 g.

A new yellow dye from 2(m-amino phenyl) 6-methyl benzothiazole sulfonic acid.

Five-tenths g. of the above sulfonic acid were dissolved in 0.1 g. NaOH and 100 cc. of water. The solution was kept at 10–15°, and treated with a solution of NaOCl, consisting of 0.5 g. of bleaching powder in the calculated amount of sodium carbonate solution. This is the method described in the German patent[7] for making Columbia Yellow from the monosulfonate of dehydrothio-*p*-toluidine. The violet solution became cloudy and took on a wine red color. After standing for 24 hours, the product was precipitated with dilute sulfuric acid. Drying produced a brown powder. A small amount of this gives a deep red color with conc. sulfuric acid.

Comparative dyeing tests using 2% strength of dye solution on cotton, showed that the yellow dye obtained was a much lighter shade than Columbia Yellow. The dye is fast to acids and alkalies.

2(o-Nitro phenyl) 6-methyl benzothiazole.

Two g. of the zinc salt were dissolved in 5 cc. of glacial acetic acid and 2 cc. of *o*-nitrobenzoyl chloride added. There was apparently no reaction in the cold, so the solution was heated for $^1/_2$ an hour in a boiling water bath. The solution was poured into water and the precipitate filtered off. This low melting solid was warmed with N NaOH for an hour, after which it became tarry. Attempts to crystallize it have so far failed. When distilled in *vacuo* a yellow gum was obtained. Yield of gum 0.9 g. or 57%.

If *o*-nitrobenzoyl chloride by itself is mixed with the zinc salt, the reaction goes with explosive violence, leaving a charred mass.

2(o-Amino phenyl) 6-methyl benzothiazole.

One g. of the above *o*-nitro benzothiazole was boiled with 10 cc. of conc. HCl, 90 cc. of water and 10 g. of granulated tin for three hours. The product was contained mostly in the form of a salt which remained insoluble in the acid solution. This precipitate was filtered off and warmed with strong NaOH. The amine crystallized from alcohol in rosettes of snow white needles, m. p. 137° corr. Yield 0.7 g. or 62%. It showed a blue fluorescence in alcohol and acetone. Readily soluble in alcohol, acetone, benzene, chloroform, carbon disulfide, ether, and carbon tetrachloride.

Combustion analysis.

Sample—0.1060 g. Water—0.0485 g. CO_2—0.2717 g.
Calc. for $C_{14}H_{12}N_2S$: C—70.00%, H—5.00%
Found: C—69.90%, H—5.12%

2(o-Acetamino phenyl) 6-methyl benzothiazole.

One g. of 2(*o*-amino phenyl) 6-methyl benzothiazole was warmed with 2 cc. of acetic anhydride. Solution took place on mixing. The mixture was poured into water and the solid recrystallized from alcohol, giving colorless needles, m. p. 150° corr. Readily soluble in alcohol, ether, benzene. Yield 0.9 g. or 77%.

Combustion analysis.

Sample—0.0839 g. Water—0.0365 g. CO_2—0.2081 g.
Calc. for $C_{16}H_{14}ON_2S$: C—68.08%, H—4.96%
Found: C—67.64%, H—4.87%

Sulfonation of 2(o-amino phenyl) 6-methyl benzothiazole.

One g. of 2(*o*-amino phenyl) 6-methyl benzothiazole was sulfonated with fuming sulfuric, as previously given for the meta isomer. The product of the sulfonation when poured upon ice, gave a gelatinous precipitate. The solution of the sodium salt was a deep blue color which turned to a dark green on acidifying, the color of the gelatinous sulfonic acid. Drying in the oven produced a black hard solid. Yield 0.8 g.

Attempt to form a dye analogous to Columbia Yellow from the above.

The hypochlorite was carried out exactly as described for the meta isomer. The blue solution did not change in color on standing over night with the hypochlorite mixture. The product when precipitated with dilute acid and dried, gave a black solid. 0.8 g. of the sulfonic acid gave 0.6 g. of the solid. Dyeing tests using a 2% solution of this solid did not produce any color on unbleached cotton. The solid dissolved in concentrated sulfuric acid to form a solution with a light red tinge, whereas the meta and para isomers had produced deep carmine red solutions.

Coupling thio- and dithio-p-toluidine with "H" acid.

One and eight-tenths g. of thio-*p*-toluidine were dissolved in 1 cc. conc. HCl and about 20 cc. of boiling water. The solution was cooled to 0° with ice, 20 cc. of conc. HCl added, and then a solution of 0.72 g. of sodium nitrite slowly poured in until a blue reaction was obtained with iodide starch paper. The clear azo solution was added slowly to a cold solution of 3.5 g. of "H" acid in 3.5 g. sodium carbonate and 40 cc. of water. When all was added the mixture generally gave an alkaline reaction, and if it did not, more sodium carbonate was added. After stirring for 15 minutes the whole was heated to 80°, salt added until the dye comes out, then filtered and dried. Yield about 3 g. Does not dye cotton directly but gives a very good dark purple on wool. It is very fast to light, soap, acids, and alkali.

Dithio-*p*-toluidine when coupled with "H" acid in the same way as the above, gave a dye with the same properties but of a lighter shade.

Although only a portion of the fusion residue went into solution when treated with nitrous acid, the diazonium solution thus produced, when coupled with "H" acid, gave a similar dye of lighter shade.

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BIOGRAPHICAL

Leonard Smidth was born in Schulenburg, Texas, July 4, 1899. After attending the public schools of Houston, he entered Rice Institute in 1917, receiving the degree of B.A. in 1921. He became connected with the Western Electric Co. in Chicago, and after attending their engineering school was sent to New York City. There he entered Columbia University and still retaining his position with the above company, received his M.A. in chemistry, in February, 1923. Returning to school in October, 1923, he has been doing work under the Faculty of Pure science. He held the Du Pont fellowship for the year 1923–24, and served as an assistant in Chemistry during 1924–25. He is a member of Sigma Xi.